INSTITUTE OF PHYSICS PUBLISHING NANOTECHNOLOGY
Nanotechnology **13** (2002) 314–317 PII: S0957-4484(02)30998-X

Scanning force microscopy three-dimensional modes applied to the study of the dielectric response of adsorbed DNA molecules

C Gómez-Navarro[1], A Gil[1,3], M Álvarez[1,4], P J De Pablo[1,5], F Moreno-Herrero[1], I Horcas[1], R Fernández-Sánchez[2], J Colchero[1], J Gómez-Herrero[1] and A M Baró[1]

[1] Laboratorio de Nuevas Microscopías, Departamento de Física de la Materia Condensada Universidad Autónoma de Madrid, E-28049 Madrid, Spain
[2] Nanotec Electrónica SL Padilla 1, E-28036 Madrid, Spain

Received 20 November 2001, in final form 25 March 2002
Published 23 May 2002
Online at stacks.iop.org/Nano/13/314

Abstract
We have developed a set of working modes for scanning probe microscopy (SPM), which generalizes the usual method of acquiring data. We call these modes three-dimensional (3D) modes. Using these modes it is possible to measure typical SPM magnitudes, such as, for example, the tunnel current, the normal force and the amplitude or frequency of the cantilever oscillation, as a function of any other two magnitudes of the system: $f(x_1, x_2)$. In this paper we present different examples of 3D modes. In particular, we have applied 3D modes to the study of the electrostatic interaction of co-adsorbed single walled carbon nanotubes and individual DNA molecules with a metallic scanning force microscopy tip. The data indicate that adsorbed DNA has a dielectric constant similar to that of the glass substrate.

1. Introduction

Scanning probe microscopy (SPM) [1, 2] is a powerful technique that provides images with atomic resolution. In addition, SPM can be used to study the different physical properties of a sample. In this respect, magnitudes related to the density of states, the barrier height, the adhesion and stiffness among others can be measured. A number of different modes have been developed to measure those magnitudes: current image tunnelling spectroscopy (CITS) [3], jumping [4] and pulsed force microscopy [5], force volume [6], etc. In this paper we introduce a very general procedure that we have called three-dimensional (3D) modes [7]. These modes allow us to measure a magnitude of the SPM system as a function of two other magnitudes: $f(x_1, x_2)$ where f can be the normal force exerted on the cantilever, the lateral force, the oscillation amplitude, the tunnelling current between a tip and a sample etc, while x_1 and x_2 can be the tip–sample distance, the tip–sample bias voltage, the lateral x–y position or the oscillation frequency of the cantilever. As examples of 3D modes we report on experimental data of the effects of an electrostatic field on the oscillation amplitude, $A(\omega, z)$, of a scanning force microscopy (SFM) cantilever as a function of its oscillation frequency ω and the tip–sample distance[6] z and on the normal force $F_N(z, V)$, as a function of the tip–sample distance and the tip–sample bias voltage. Finally, we present measurements of the electrostatic interaction between a SFM metallic tip and a glass substrate having co-adsorbed single walled carbon nanotubes (SWNT) and double-stranded DNA molecules. In this case, the measured function is $\delta\omega(x{-}y, z)$ where $\delta\omega$ is the

[3] Present address: CMP Cientifica, 28230 Las Rozas, Madrid, Spain.
[4] Present address: Grupo de Biosensores, Instituto de Microelectronica de Madrid, IMM-CSIC, 28760 Tres Cantos, Madrid, Spain.
[5] Present address: Physics of Complex Systems, Division of Physics and Astronomy, Vrije University, de Boelelaan 1081, 1081 HV, Amsterdam, The Netherlands.

[6] More precisely, z corresponds to the piezoelectric elongation along the perpendicular direction of the sample.

shift of the resonance frequency of the SFM cantilever and x–y is the lateral position along a line on the surface plane of the sample.

2. Description of the method

The heart of the microscope used in the experiments is a digital signal processor (DSP) board that performs the real time data acquisition task, and generates a number of signals including the scanning signal, the bias voltage, etc. The basic SPM scanning mode, measures and displays a magnitude of the system as a function of the x, y tip position $f(x, y)$, for example the topography or the lateral force. Modern SPM systems are able to measure and show several SPM magnitudes simultaneously in real time using a pseudocolour-type rendering. By applying a matrix transformation the image can be rotated and hence it will be a function of $f(x(\theta), y(\theta))$. Due to the scanning image formation, the displayed function always depends on a fast magnitude and a slow magnitude. We always note the first magnitude as the fast scan direction, and the second as the slow scan direction. For example, in the previous case $x(\theta)$ is the fast scan signal and $y(\theta)$ the slow one. Three-dimensional modes are a generalization of this geometric scan, i.e. a 3D-mode image is a plot of a magnitude $f(x_1, x_2)$ where x_1 is the fast scan signal and x_2 is the slow scan signal. For any 3D mode, x_1 and x_2 are output signals of the DSP which can have different physical meanings depending on the experimental set-up (see figure 1 for an explanation). For example, x_1 and x_2 can correspond to a given spatial direction parallel to the surface plane of the sample x–y, the perpendicular direction to the surface plane of the sample z, the bias voltage V or, in the case of SFM, the cantilever resonance frequency ω. While 3D modes are a general tool in SPM, for the sake of clarity we focus its description and application on SFM. Three-dimensional modes can be totally implemented by software. The following possibilities have already been tested: $f(x$–$y, z)$, $f(x$–$y, V)$, $f(z, V)$, $f(x$–$y, \omega)$, $f(z, \omega)$ and all possible permutations of fast and slow scan signals. The 3D-mode maps are displayed in real time as any conventional image. As in the case of usual geometric scan modes, several magnitudes can be simultaneously measured and displayed.

3. Experimental results and discussion

Figure 2 shows the effect of an electrostatic field on different SFM magnitudes. In figures 2(a) and (b) we present the cantilever oscillation amplitude A for different driving frequencies ω at different tip–sample distances z: $A(\omega, z)$. The fast scan signal shows the oscillation frequency, the slow scan signal corresponds to the z displacement and the height represents the oscillation amplitude [8, 9]. To perform this measurement, a metal-coated tip, biased 8 V with respect to the glass substrate, was oscillated near the sample's surface. For each value of the vertical tip position z, the oscillation frequency was swept through a range of values around the resonance frequency. As the tip approaches the sample surface, a shift in the resonance frequency is clearly seen, since the maximum of the oscillation amplitude moves towards lower frequencies. The frequency shift is a consequence of the electrostatic interaction produced by the +8 V bias voltage applied between the metal-coated SFM tip and the surface [10].

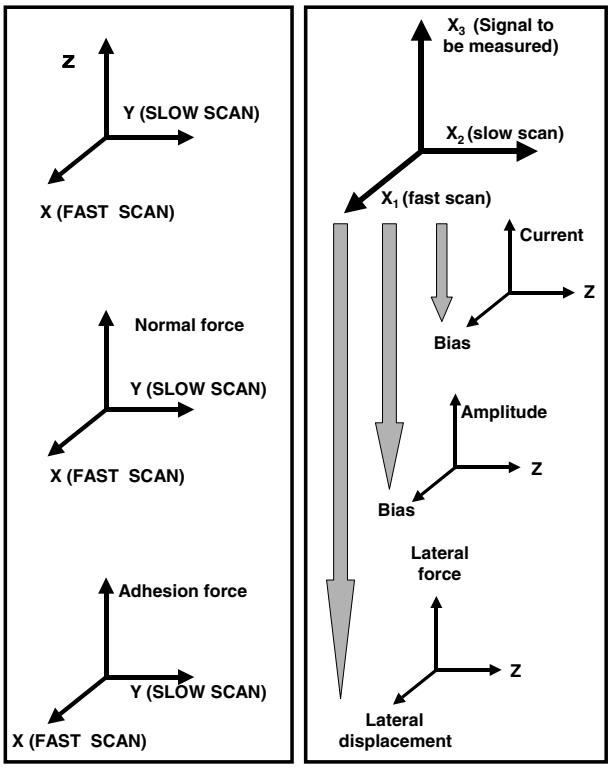

Figure 1. Schematic diagram showing the different options for geometric scan modes (left frame) and 3D modes (right frame). As can be seen, the 3D modes are a generalization of classical geometric modes.

As a result of this 3D-mode experiment, very precise data of the interaction are obtained in a fast and easy way. A detailed analysis of the measured frequency shift allows us to study the interaction potential between tip and sample. If the interaction force $F(z)$ can be assumed to vary linearly over the range of cantilever oscillations, then the resonance frequency ω_0 as a function of distance is [11, 12]

$$\omega_0(z) = \omega_{00}\sqrt{1 + \frac{1}{c_{lever}}\frac{\partial F}{\partial z}(z)}$$

where ω_{00} corresponds to the resonance frequency of the free cantilever, c_{lever} is the force constant of the cantilever and $F(z)$ is the interaction force. The effect of the electrostatic interaction on the normal force as a function of the tip–sample distance and the tip–sample bias voltage $F_N(z, V)$ is shown in figure 2(c). The minimum on the normal force corresponds to the SFM tip snap-in. At these points the gradient of the attractive force exceeds the spring constant of the cantilever which leads to an instability [13]. For a small bias voltage (upper region of the 3D plot) no large distance interaction is presented and hence the instability is caused by a short-range interaction, such as van der Waals or capillarity forces. For a large bias, the electrostatic interaction is felt by the cantilever at large distances introducing a soft curvature in the force versus distance plots and a shift in the position of the minimum.

Figure 3(a) is a non-contact SFM topographic image showing a SWNT and a DNA molecule co-adsorbed on a glass substrate. The sample was prepared by pre-treating the substrate with 3-aminopropyltriethoxysilane (APTES) and immersing them in a 0.1% volume of APTES for 15 min. Then,

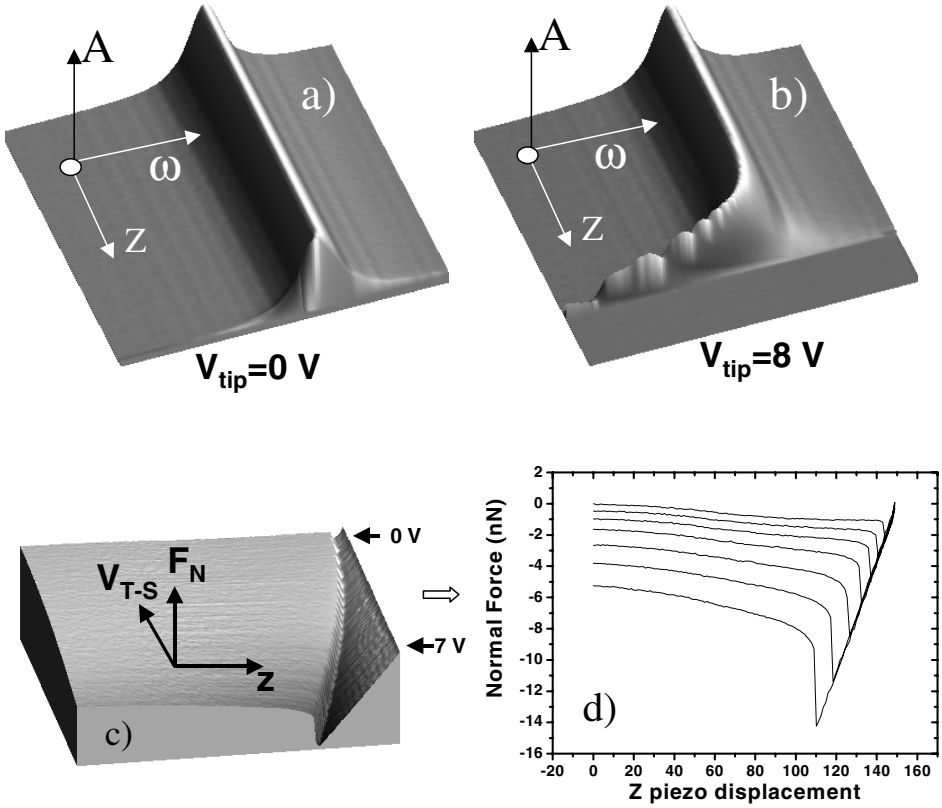

Figure 2. (a) and (b) Representation of the oscillation amplitude A as a function of the driving frequency ω (fast scan direction) and the tip–sample distance z (slow scan direction) $A(\omega, z)$. In (a) no bias voltage is applied between tip and sample. Therefore, no frequency shift is observed until the tip is just a few nanometres away from the surface (short-range interaction). In (b) a bias voltage of 8 V is applied between tip and sample, and a clear frequency shift is observed for large tip–sample distances showing the long-range interaction characteristic of the electrostatic forces. (c) and (d) show the effect of a long-range interaction in the vertical deflection of the cantilever measured as a function of the tip–sample distance and the bias $F_N(z, V)$. (c) shows a 3D rendering of $F_N(z, V)$, the bias voltage is varied between 0 and 7 V and the total displacement along the z-direction is 150 nm. In (d), several profiles extracted from (c) are shown. The profiles are taken at 0, 2, 3, 4, 5, 6 and 7 V. The long-range interaction (electrostatic field) produces the curvature of the $F_N(z)$ plots as the bias is increased.

the samples were rinsed with 2-propanol, ultrapure water and dried with nitrogen [14]. A solution of λ-DNA and SWNT was dropped over the substrates and allowed to bind for one hour. Finally, the samples were washed with water and dried. Concentrations of DNA and SWNT were adjusted by SFM inspection until a final concentration of about one λ-DNA molecule and 5–10 SWNT/μm^2 was obtained. As in the previous example a metal-coated tip is used in the experiment. In order to study the dielectric response of the molecular wires we have performed a 3D-mode map.

The measured magnitude is the output of a phase locked loop (PLL) that keeps the system at its resonance frequency. Hence, we measure the resonance frequency shift $\delta\omega$ induced by the tip–sample interaction in the cantilever oscillation. The scanning magnitudes are the lateral tip displacement x–y (fast scan) and the vertical piezoelectric displacement z (slow scan). Figure 3(b) shows the 3D mode $\delta\omega(x$–$y, z)$ along the white line drawn in figure 3(a). A bias voltage of +6 V was applied between tip and sample during the acquisition of the map. For long tip–sample distances (lower lines in figure 3(b)) the electrostatic interaction is negligible and therefore no frequency shift is detected. As the tip approaches the surface, a general decrease of the resonance frequency is observed due to the electrostatic force gradient produced by the polarization of the glass substrate. At the position of the SWNT, however, the electrostatic force gradient is different, resulting in a decrease of the resonance frequency. This effect increases with the applied tip–sample bias voltage. No contrast is detected at the position of the DNA molecule for tip–sample bias voltages between ±10 V. Figure 3(c) presents a profile performed along the white line drawn in figure 3(b), showing a clear electrostatic signal localized over the SWNT. Since the electrostatic force gradient between the SFM tip and the sample is basically produced by the effect of the polarization induced by the bias voltage, the absence of a signal over the DNA molecule implies that the dielectric constant of the DNA and the substrate are similar. In contrast, the SWNT is a good conductor and hence its dielectric constant is very high (in a perfect 3D conductor it would be infinite), inducing a strong electrostatic contrast with respect to the insulating substrate. This result is especially significant since it has been obtained without contact to any electrode[7].

The dielectric nature of DNA strongly disagrees with data reported by other authors [15, 16], since our experiments suggest an electrical resistance similar to that of the insulating substrates. A first principle calculation performed in poly(C)–poly(G) DNA shows a band structure typical of a semiconductor [17] but in the λ-DNA case the disorder introduced by

[7] A detailed discussion of these results has been submitted to PNAS.

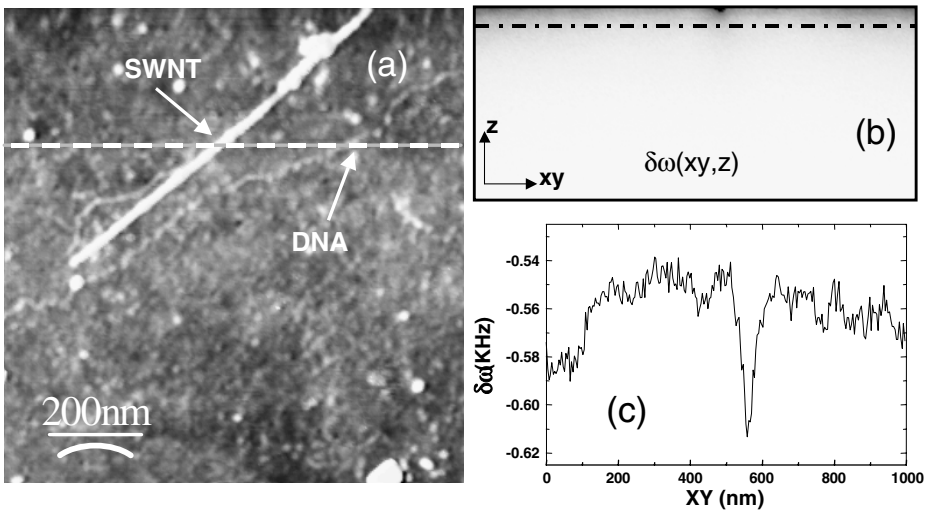

Figure 3. (a) Topographic image of a SWNT and an individual λ-DNA molecule on a glass substrate. (b) is a pseudocolour-type image of the frequency shift as a function of z (slow scan direction, vertical axis) and the lateral displacement xy. The lateral displacement was performed along the white line shown in (a). (c) shows the profile taken along the dotted line in (b). A significant decrease is observed above the SWNT, whereas no change appears above the DNA molecule. The profile was taken with the tip placed at 15 nm above the surface.

the random base sequence entirely destroys the band structure. Electrical transport based on polarons has been put forward as a second mechanism for DNA conductivity. Since polarons are associated with phonons when adsorbing DNA molecules on a surface the degrees of freedom are significantly reduced and so are the phonons. Therefore, one would expect a parallel decrease in the conductivity based on polarons. Quantitative analyses of the reported data are currently in progress.

In summary, a generalized set of SPM modes, called 3D modes, has been introduced. The 3D modes allow characterization of the tip–sample interaction in an easy and precise way. Three examples of 3D modes have been reported. The first is a map of the cantilever oscillation amplitude as a function of the driving frequency ω and the tip vertical displacement z. The second example is a map of the normal force as a function of the tip–sample distance and the tip–sample bias voltage $F_N(z, V)$. Finally, the third example shows the shift of the resonance frequency as a function of the lateral displacement and the piezoelectric elongation. Both implementations of 3D modes have been used to study the electrical response of the SWNT and DNA molecule. By comparing the electrostatic signal of the SWNT and DNA we conclude that DNA has a dielectric constant similar to that of the substrate.

Acknowledgments

The authors acknowledge M T Martínez, W K Maser and A M Benito for their help in the sample preparation procedures. We would also like to thank J J Sáenz and S Gómez-Moñivas for interesting discussions. F Moreno-Herrero is supported by a fellowship from Comunidad Autónoma de Madrid. Financial support is acknowledged from Ministerio de Educación y Ciencia through project MAT2001-0664, as well as from the FGUAM through the project Nanodigital 4750.

References

[1] Binnig G, Rohrer H, Gerber Ch and Weibel E 1982 *Phys. Rev. Lett.* **49** 57
[2] Binnig G, Quate C F and Gerber C 1986 *Phys. Rev. Lett.* **56** 930
[3] Hamers R J, Tromp R M and Demuth J E 1986 *Phys. Rev. Lett.* **56** 1972
[4] De Pablo P J, Colchero J, Gómez Herrero J and Baró A M 1998 *Appl. Phys. Lett.* **73** 3300
[5] Rosa A, Weilandt E, Hild S and Marti O 1997 *Meas. Sci. Technol.* **1**
[6] Van der Werf O, Putman C A J, Groth B G and Greve J 1994 *Appl. Phys. Lett.* **65** 1195
[7] Colchero J, Storch A, Gómez-Herrero J and Baró Vidal A M 1998 *Langmuir* **14** 2230–4
[8] Gady B, Schleef D and Refenberger R 1996 *Phys. Rev.* B **53** 8065
[9] Dürig U, Gimzewski J K and Pohl D W 1986 *Phys. Rev. Lett.* **57** 2403
[10] De Pablo P J, Gómez-Navarro C, Gil A, Colchero J, Martínez M T, Benito A M, Masser W K, Gómez-Herrero J and Baró A M 2001 *Appl. Phys. Lett.* **79** 2979
[11] Cleveland J P, Mann S, Bucek D and Hansma P K 1993 *Rev. Sci. Instrum.* **64**
[12] Dürig U, Züger O and Stalder A 1992 *J. Appl. Phys.* **72** 1778
[13] Meyer E, Heinzelmann H, Grütter P, Jung Th, Weisskopf Th, Hidber H R, Lapka R, Rudin H and Güntherodt H J 1988 *J. Microsc.* **152** 269
[14] Burghard M, Duesberg G, Guenther P, Muster J and Siegmar R 1998 *Adv. Mater.* **10** 584
[15] Lintao Cai, Hitoshi Tabata and Tomoji Kawai 2000 *Appl. Phys. Lett.* **77** 3105
[16] Kasumov A Y, Kociak M, Guéron S, Reulet B, Volkov V T, Klinov D V and Bouchiat H 2001 *Science* **291** 280–2
[17] De Pablo P J, Moreno Herrero F, Colchero J, Gómez Herrero J, Herrero P, Baró A M, Ordejón P, Artacho E and Soler J M 2000 *Phys. Rev. Lett.* **85** 4992–5